

ELECTROTHERMAL ANALYSIS: A NEGLECTED THERMAL ANALYSIS TECHNIQUE?

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ABSTRACT

This is a review of the electrothermal analysis (ETA) techniques used in this author's laboratory during the past 10 - 14 years. Most of the ETA techniques employed the detection and measurement of the d.c. or a.c. current flow through the sample as a function of temperature. These measurements, at constant EMF, varied with the change of resistance of the system; the latter being dependent on the nature of the thermal reaction being investigated. A new technique, thermovoltic detection (TVD), in which the EMF of the reacting system in contact with two dissimilar electrodes is recorded as a function of temperature, is also described.

INTRODUCTION

According to the International Confederation of Thermal Analysis (ICTA), the thermal analysis technique of thermoelectrometry is defined as "a technique in which the electrical characteristics of a substance is measured as a function of temperature whilst the substance is subjected to a controlled temperature programme."<sup>[1]</sup> The most common measurements, according to ICTA, are of resistance, R, conductance,  $\Delta$ , and capacitance, C. However, since  $\Delta = 1/R = I = E/R$ , and E is usually constant,  $\Delta = I = k/R$ ; thus many investigations report the use of current, I, plotted as a function of temperature. Indeed, David [2] used the term "amperometric thermal analysis" (ATA) to describe the technique that he developed.

In a recent survey of thermal analysis techniques [3], it was found that thermoelectrometric techniques accounted for 2.2% of the techniques reported for a total of 465 papers in Thermochimica Acta, and 1.4% in the J. of Thermal Analysis. This is less than 1% of the 29.1 and 22.0% reported for TG, in the same journals, respectively. Thus, these techniques are not widely used in thermal analysis; they could be described here as "lesser-used" or perhaps "neglected" thermal analysis techniques.

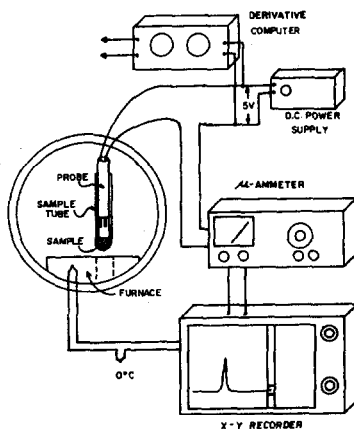
The thermoelectrometric or electrothermal analysis techniques described here are those that are primarily the result of work done in this author's laboratory during the past 10 - 14 years. Most of the investigations concern the detection and measurement of the d.c. or a.c. current passing through the sample at a constant applied voltage, although a voltage measurement technique is also described

(thermovoltaic detection).

#### ETA IN THIS LABORATORY

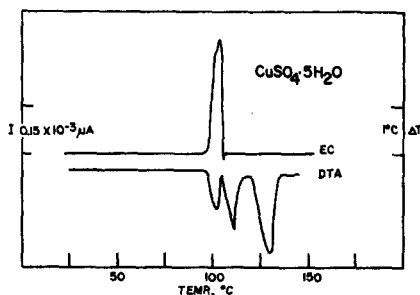
The first use of ETA in this laboratory was to detect the presence of quadruple points in metal salt hydrates systems in 1968 [4]. At the quadruple point, for a system such as  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , four phases can coexist:  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}(s)$ ,  $\text{H}_2\text{O}(l)$  and  $\text{H}_2\text{O}(g)$ . Due to the presence of a liquid phase in contact with the ionic solid, a low resistance or conducting solution is obtained so that a rapid increase in  $I$  is indicative of the quadruple point. The ETA apparatus employed for these studies is shown in Fig. 1, consisted of the usual ar-

Fig. 1. Schematic diagram of ETA apparatus [4].



rangement of sample holder, probe and furnace, a d.c. power supply, a recording micro-ammeter and a recording system (X-Y plotter). To facilitate sample changing, the sample was contained in a glass tube into which the two electrode probe was inserted. Thus, as the liquid water phase of the system increased, current flow through the sample also increased. This increase was detected and recorded as a function of sample temperature. The apparatus was used to detect the quadruple points of the  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , and  $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$  systems. To illustrate its use, the DTA-ETA curves of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  are presented in Fig. 2. The DTA curve for  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was similar to that previously described

Fig. 2. DTA and ETA curves of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  [4].

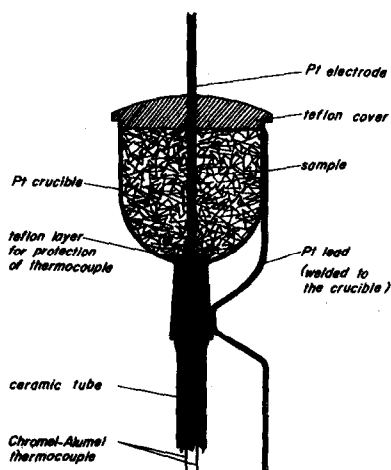


except for the more pronounced resolution of the first endothermic peak. The

first peak began at about 91°C, with a  $T_{\min}$  (peak minimum temperature) of 101°C. The  $T_{\min}$  values for the second and third peaks were 112 and 135°C, respectively. Formation of liquid water was readily shown by the ETA curve in that the current flowing through the sample began to increase at about 95°C and obtained a maximum,  $ETA_{\max}$ , at 103°C. Rapid vaporization of the liquid water from the saturated salt solution was readily apparent by the steep slope of the descending portion of the curve. No ETA peak was observed for the  $CuSO_4 \cdot 3H_2O \rightarrow CuSO_4 \cdot H_2O$  transition.

A more elaborate apparatus was constructed by Halmos and Wendlandt [5] in 1973 which permitted simultaneous ETA-DTA measurements. A cross-sectional view of the sample holder is given in Fig. 3. The sample holder, constructed from a

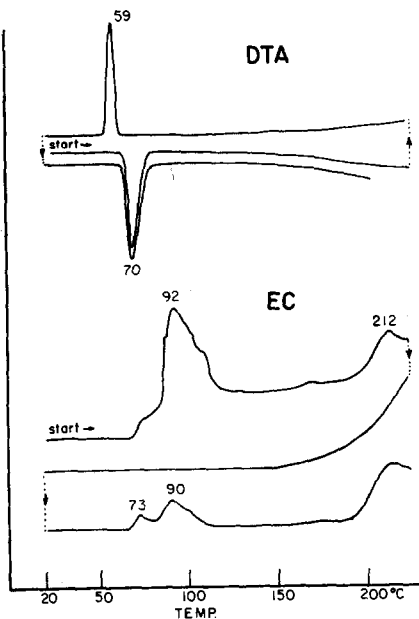
Fig. 3. ETA-DTA sample holder [5].



platinum crucible, 5 mm in diameter and 5 mm in height, rested on a thermocouple junction located on the apparatus. To detect the ETA, one electrode was welded to the sample container while the other was a platinum wire which was introduced into the sample through a hole in the Teflon cover. The depth of the sample contact of this electrode was adjustable by means of a screw device. This apparatus was used to detect and measure quadruple points in  $CuSO_4 \cdot 5H_2O$  and  $[Co(NH_3)_5H_2O]Br_3$  and also for ETA-DTA measurements of thermochromic compounds.

The order - disorder transition for a series of thermochromic  $M_n HgI_4$  complexes, where M is  $Ag^+$ ,  $Cu^+$ ,  $Hg_2^{2+}$ ,  $Tl^+$  and  $Pb^{2+}$ , were studied by the above ETA-DTA apparatus [6]. As an example, the ETA-DTA curves for  $Cu_2 HgI_4$  are given in Fig. 4. As is well known, the thermochromic transition of this compound

Fig. 4. DTA and ETA curves of  $\text{Cu}_2\text{HgI}_4$ ; heating and cooling modes indicated [6].

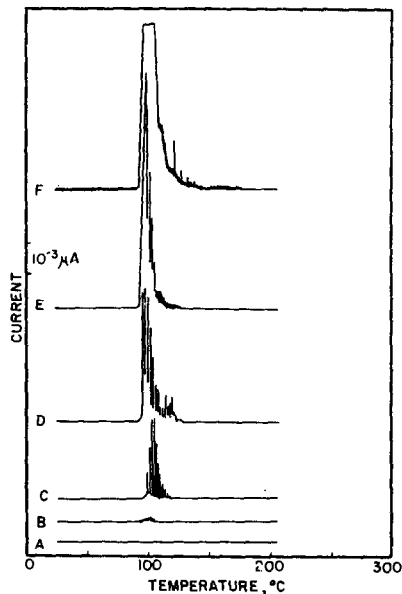


occurs at about 70°C, at which temperature the color change is from red to brown-black. The color transition is reversible in that on cooling, the red compound is again obtained. In the DTA curves, in both the heating and cooling modes, only a single narrow endothermic peak was observed, which was due to the thermochromic transition. During both heating curves, the peak began at 64°C with a  $T$  minimum temperature of 70°C. The peak was also observed during the cooling mode, indicating, as expected, that the transition is reversible. The ETA curve peak was not as well pronounced during the thermochromic transition as was the DTA peak. Only a shoulder peak was observed simultaneously with the DTA curve peak but this was followed by a large asymmetric curve peak with a maximum at approximately 92°C. Apparently, additional disorder occurs about 200°C which results in a curve peak with a maximum at about 212°C. On cooling, none of the initial ETA peaks were observed in the curve. Reheating the sample gave the same ETA curve peaks but all of them were at a decreased peak height. From the above data, the ETA curves appear to indicate multiple disordering processes or transitions involving phases not previously reported. Similar behavior was noted for the other complexes as well as for  $\text{HgI}_2$  and  $\text{AgI}$ .

In conjunction with the development of a high pressure thermobalance [7] and DTA apparatus [8], an ETA apparatus capable of operation from 1 to 170 atm in the temperature range of 25 to 500°C was also constructed [9]. The sample holder, electrode system, and furnace were enclosed by a stainless-steel pressure vessel. Pressurization of the vessel was effected by use of compressed nitrogen

gas obtained from a cylinder. The effect of pressure changes from 1 to 170 atm on the ETA curves of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  are given in Fig. 5. A moderately packed sample

Fig. 5. Effect of pressure on ETA curves of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ .  
A, 1 atm; B, 7 atm;  
C, 15 atm; D, 27 atm;  
E, 42 atm; F, 170 atm [9].



of the compound showed no change in current flow during heating at one atm. As the pressure increased, a slight change in the curve near 100°C was observed. With increasing system pressure, the magnitude of the peak height and also the area increased as did the temperature range of ETA. The increase in the peak height and area is thought to be due to the decrease in diffusion of water vapor from the sample as the pressure is increased. A second peak was not observed because the heat transfer through the metal sample cup wall was rapid enough to vaporize the liberated water and the short diffusion path was not as effective in retarding the escape of the vapor as in the previous sample holders. Additional ETA curves for  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  were given by Williams and Wendlandt [10].

In order to investigate the ETA of pure substances or mixtures of pure substances with a matrix material such as KBr, KI or KCl, a new ETA apparatus was developed [11]. The sample, in the form a disk 5 mm in diameter by 1 mm thick, was placed between two circular metal electrodes. In order to assure efficient contact between the electrodes and the sample disk, the upper electrode was held in place by a spring-loaded mechanism. Also, instead of measuring a d.c. current through the sample, a variable frequency a.c. power supply was employed which permitted a.c. current measurements of the samples.

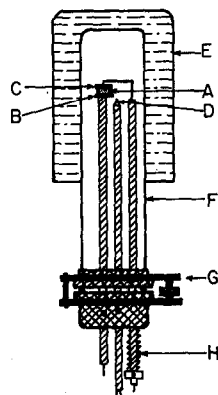
The use of simultaneous TA measurements is a well established procedure in

modern thermal analysis equipment. These measurements, such as TG-DTA, TG-DTG-DTA, and so on, can easily be made. Wendlandt [12] developed a system using a commercial thermal analysis instrument in which ETA-TG measurements can be made on two different samples. This type of arrangement permitted concurrent measurements (two or more techniques on two or more samples) rather than simultaneous measurements (two or more techniques using a single sample). For ETA-TG measurements, an additional sample holder and electrode system was inserted into the outboard end of the thermobalance furnace chamber and positioned as close as possible to the sample container [12,13]. Thus, using two different samples of the same compound, ETA and TG curves could be obtained.

A modification of this apparatus has also been described [14]. This apparatus, which used a cylindrical furnace, contained an ETA sample probe on one end while the other end contained the DTA sample probe. Thus, concurrent ETA-DTA measurements could be made on two different samples.

A high temperature ETA furnace and sample holder (for use up to 1000°C) has also been constructed [15]. The sample holder and furnace arrangement are shown in Fig. 6. The sample A, in the form of a pressed disk (1 mm x 5 mm) was

Fig. 6. ETA sample holder and furnace for use up to 1000°C [15].



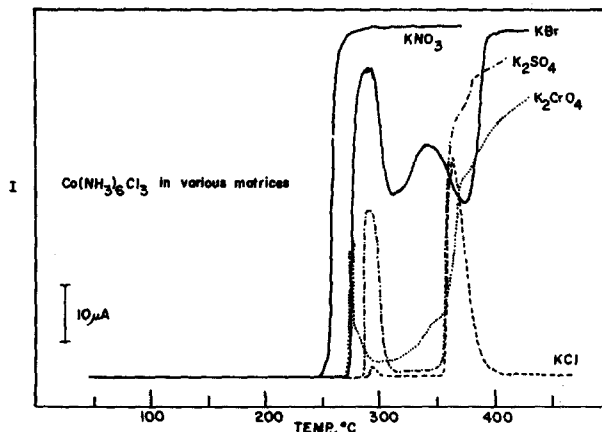
placed between two platinum electrodes (7.0 mm in diameter). Leads to the electrodes were led out of the furnace area by one-holed ceramic insulator tubes. To maintain a constant tension on the sample disk by the electrodes, one electrode is spring loaded at H. The furnace consists of a Nichrome resistance wire heater element wound on a Vycor tube suitably insulated with a ceramic material. A clamp G secures the tube furnace to the base. Furnace temperature,  $T_F$ , is detected by a Chromel-Alumel thermocouple located at D. The other components of the EC apparatus are the same as those previously described. The apparatus was used on pure samples, compressed in the form of disks, or of a matrix mixture with KCl, KBr, or KI.

Most of the ETA studies in this laboratory have been concerned with inorganic compounds, usually metal salt hydrates. Because of the complexity of the ther-

mal decomposition reactions of transition metal ammine complexes [16], ETA was also used to determine the presence of liquid or semi-liquid phases formed. One such investigation [17] involved the ETA of selected  $[\text{Co}(\text{NH}_3)_6]\text{X}_3$  and  $[\text{Co}(\text{en})_3]\text{X}_3$  complexes ( $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{HSO}_4^-$  and  $1/2 \text{C}_2\text{O}_4^{2-}$ ). These compounds, which had been previously studied by TG, DSC, MS, EGD, EGA and thermomagnetic analysis techniques, were chosen because of questions concerning the intermediates formed during the thermal dissociation processes. Also, the reaction with various matrix materials such as  $\text{KNO}_3$ ,  $\text{KBr}$ ,  $\text{K}_2\text{SO}_4$  and so on, could also be investigated.

The ETA curves of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  in various matrices are given in Fig. 7.

Fig. 7. ETA curves of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  in 1:1 matrices of  $\text{KNO}_3$ ,  $\text{KBr}$ ,  $\text{K}_2\text{SO}_4$ , and  $\text{KCl}$  [17].

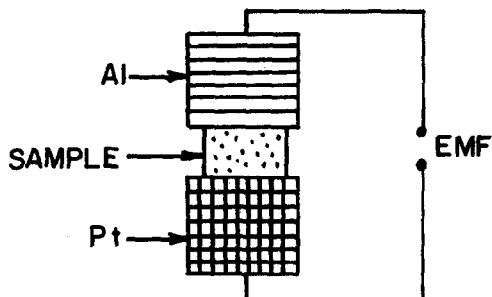


As can be seen, there is a wide variation in the ETA curve of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  with composition of the matrix material. The ETA increase begins at the following temperatures for each matrix: 250°C ( $\text{KNO}_3$ ); 270°C ( $\text{KBr}$  and  $\text{K}_2\text{CrO}_4$ ); 285°C ( $\text{K}_2\text{SO}_4$ ) and 290°C ( $\text{KCl}$ ). All of the matrix materials exhibited intermediate peaks in the ETA curve except  $\text{KNO}_3$ , which gave only a pronounced increase in EC to a maximum value of 100 A. The ETA curves all increased with temperature in the 400°C temperature range except that for the  $\text{KCl}$  matrix. Unfortunately, it is not possible at this time to interpret the reactions responsible for the occurrence of the ETA curve peaks in the  $\text{KCl}$ ,  $\text{KBr}$ ,  $\text{K}_2\text{CrO}_4$  and  $\text{K}_2\text{SO}_4$  matrices. All of the peaks are related, of course, to the formation of conducting phases formed as intermediates in the thermal dissociation reactions.

In 1980, a new ETA technique was developed [18] in which the EMF generated by a thermal decomposition reaction was recorded as a function of sample temperature. This technique, which was called "thermovoltaic detection" (TVD), has been used to characterize a wide variety of inorganic, organic and polymeric substances. The EMF is generated by the sample undergoing a thermal transition (fusion, thermal dissociation, etc.) in contact with two dissimilar electrodes

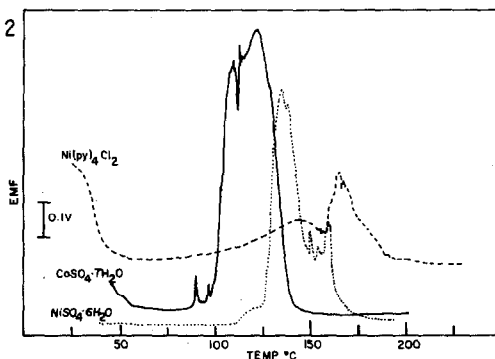
(usually platinum and aluminum, respectively), as shown in Fig. 8. The magnitude

Fig. 8. Schematic diagram of TVD electrode arrangement [20].



of the EMF signal is surprising in that it varies from 0 to 1.2 volts. Most TA techniques, it will be recalled, detect and/or record microvolt or millivolt signals, as generated by some physical parameter of the system. Thus, to record signals of this magnitude as a function of temperature, a less complex apparatus could be employed. The TVD curves of these typical compounds are shown in Fig. 9. Two of the compounds are metal salt hydrates,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ,

Fig. 9. TVD curves of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{Ni}(\text{py})_4\text{Cl}_2$  in  $\text{N}_2$  and at  $10^\circ\text{C min}^{-1}$  heating rate [18].



while the third is a pyridine complex,  $\text{Ni}(\text{py})_4\text{Cl}_2$ . For  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , a shoulder peak at  $119^\circ\text{C}$  and two peaks at  $135^\circ\text{C}$  and  $160^\circ\text{C}$ , respectively, are observed in the curve. These peak maxima agree with the concurrent DTA curve (not shown) obtained on a disk sample at the same heating rate of  $10^\circ\text{C min}^{-1}$ . In the case of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ , two major peaks are observed in the TVD curve, at  $109^\circ\text{C}$  and  $122^\circ\text{C}$ , respectively. These two peaks occurred at a much lower temperature than those found in the corresponding DTA curve ( $136^\circ\text{C}$  and  $150^\circ\text{C}$ , respectively). The evolution of water is not necessary in order to generate an EMF from the electrode system employed, as is illustrated by the TVD curves of  $\text{Ni}(\text{py})_4\text{Cl}_2$ . Two peaks are observed in the curve at  $144^\circ\text{C}$  and  $165^\circ\text{C}$ , respectively. In this temperature range the DTA curve (not shown) contained two endothermic peaks, with



peak minima at 144 and 183°C, respectively.

The thermovoltaic detector (TVD) appears to have rather general utility in the investigation of various types of thermal decomposition reaction. It has been applied to the study of the thermal decomposition of amino acids [19], organic acids [20], coordination compounds [20], polymers [20], coal [20], and others.

#### ACKNOWLEDGMENT

The financial support of this work by the Robert A. Welch Foundation, Houston, Texas, is gratefully acknowledged.

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